

# High Pressure Phase Behaviour of Binary Systems of Refrigerants and Phenylalkanes: the System 1,1,1,2-Tetrafluoroethane + Phenyloctane

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## Abstract

Vapour-liquid, liquid-liquid and liquid-liquid-vapour equilibria for the system 1,1,1,2-tetrafluoroethane + phenyloctane were determined in the temperature range from 260 to 400 K and at pressures up to 12 MPa. The system was found to be a type IV system according to the classification of Van Konynenburg and Scott. The  $(l_2=l_1)g$  upper critical endpoint of the low-temperature branch of the  $l_2l_1g$  curve was found at  $T = 352.85$  K and  $P = 2.440$  MPa. The  $(l_2=l_1)g$  lower critical endpoint of the high temperature branch of the  $l_2l_1g$  curve was found at  $T = 381.82$  K and  $P = 4.220$  MPa and the upper critical endpoint  $l_2(l_1=g)$  at  $T = 392.88$  K and  $P = 5.135$  MPa.

## Keywords:

Liquid-liquid equilibria, vapour-liquid equilibria, liquid-liquid-vapour equilibria

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## 1. Introduction

In refrigeration cycles using the new generation HFC refrigerants synthetic oils like polyol esters, polyalkylene glycols or phenylalkanes are used as lubricants [1].

Phenylalkanes have good chemical stability, high lubricity and low hygroscopy and are slightly miscible with HFC's [2]. The solubility and viscosity of some HFC + phenylalkanes systems was studied by Takigawa et al. [3].

To understand the phase behaviour of this type of refrigerant-oil systems better we decided to study the phase behaviour of binary systems of HFC refrigerants with members of the homologous series of the phenylalkanes.

In binary families of HFC refrigerants with members of the homologous series of n-alkanes [4] or phenylalkanes [5] different types of fluid phase behaviour occur. With increasing chain length of the n-alkane or phenylalkane a transition occurs from type II to type IV to type III fluid phase behaviour according to the classification of Van Konynenburg and Scott [6]. The system 1,1,1,2-tetrafluoroethane + phenylheptane was shown to be a type II system [7]. So, it is very likely that for systems of 1,1,1,2-tetrafluoroethane with higher members of the phenylalkane homologous series also a transition from type II to type III via type IV will occur.

In this paper we present experimental data on vapour-liquid equilibria, liquid-liquid equilibria and liquid-liquid-vapour equilibria for the system 1,1,1,2-tetrafluoroethane (R134a) + phenyloctane.

## 2. Experimental

The experiments were carried out according to the synthetic method using a so-called Cailletet equipment, which can be used in the temperature range  $-40^{\circ}\text{C}$  to  $240^{\circ}\text{C}$  and at pressures up to 150 bar [8]. A mixture of 1,1,1,2-tetrafluoroethane and phenyloctane with known composition is contained in the top of the Cailletet tube. This Pyrex glass capillary tube is placed in a thermostat bath filled with a water-ethanol mixture, water or a water-glycol mixture depending on the temperature range to be investigated. Phase transitions were determined visually by slowly changing the pressure at constant temperature or in the case of liquid-liquid equilibria by changing the temperature slowly at constant pressure.

The temperature of the thermostat bath was kept a constant temperature within approximately 0.03 K. The temperature was measured with a platinum resistance thermometer (uncertainty  $\pm 0.01$  K), which was calibrated against a secondary standard thermometer. The pressure was measured with dead weight pressure gauge (De Wit, uncertainty  $\pm 0.003$  MPa) or in case of the measurement of liquid-liquid-vapour equilibria with a manometer (Heise, uncertainty  $\pm 0.01$  MPa). The manometer was calibrated against the dead weight gauge.

## 3. Chemicals

The 1,1,1,2-tetrafluoroethane used was obtained from Airproducts with a minimum purity of 99.9 % (GC). The phenyloctane used was from Fluka with a minimum purity of 99 % (GC). The chemicals were used without further purification.

## 4. Results and discussion

For 10 mixtures of 1,1,1,2-tetrafluoroethane and phenyloctane liquid-liquid isopleths were determined experimentally for mole fractions of phenyloctane between 0.02 and 0.70. The data are given in Table 1 and plotted in Figure 1. These data represent upper

solution temperatures. The liquid-liquid isopleths are steep curves in the  $P,T$ -diagram. The slope of these curves changes from negative for concentrations close to the critical concentration to positive for concentrations further removed from the critical concentration. In Table 2 the liquid-liquid-vapour equilibrium data are presented. These experimental results are also plotted in Figure 1. The liquid-liquid-vapour curve consists of two branches. The low-temperature branch of this curve ends in an upper critical endpoint ( $l_2=l_1$ )g at  $T = 352.85$  K and  $P = 2.440$  Mpa, where the two liquid phases critically merge in the presence of a non-critical vapour phase. The high-temperature branch of this curve starts in a lower critical endpoint ( $l_2=l_1$ )g at  $T = 381.82$  K and  $P = 4.220$  Mpa and ends in an upper critical endpoint  $l_2(l_1=g)$  at  $T = 392.88$  K and  $P = 5.135$  MPa. In this upper critical endpoint the light liquid phase  $l_1$  and the vapour phase critically merge in the presence of the noncritical heavy liquid phase  $l_2$ . The critical point of pure 1,1,1,2-tetrafluoroethane is found at  $T_c = 374.12$  and  $P_c = 4.045$  Mpa [7, see also 9-11]. So, the high temperature branch of the binary liquid-liquid-vapour curve is located completely at temperatures above the critical point of pure 1,1,1,2-tetrafluoroethane.

Figure 2 shows the liquid-liquid equilibria in shows isobaric  $T,x$ -cross sections at 5, 7, 9 and 11 Mpa constructed by interpolation from Figure 1. The figure shows that these equilibria are not very pressure dependent, except in the critical region. From the location of the maxima of the cross sections it can be concluded that the critical concentration is almost pressure independent in the pressure range investigated. The cross sections show a temperature maximum at the critical concentration.

In Table 3 the experimentally determined bubble point pressures and liquid-liquid upper solution pressures as function of temperature for 12 mixtures of 1,1,1,2-tetrafluoroethane and phenyloctane in the temperature range 280 to 400 K are presented, together with the vapour pressure data for 1,1,1,2-tetrafluoroethane. The vapour pressure data were taken from [7] and agree within the experimental uncertainty with the data of Niesen et al. [12]. The bubble point data cover the full range of compositions. In Figure 3 some selected isopleths are plotted. From the experimental isopleths isothermal  $P,x$ -cross sections were constructed by interpolation and plotted in Figure 4. Figure 4 shows three isotherms. The isotherm at 350 K is at a temperature lower than the critical endpoint of the low temperature branch of the liquid-liquid-vapour curve. So at this temperature a liquid-liquid-vapour equilibrium is found, which is indicated by the horizontal straight line. Below this line we find  $l_2g$  equilibria, above this line two two-phase regions are found: a  $l_1l_2$  region roughly between  $x \approx 0.1$  and  $x \approx 0.33$  and a  $l_1g$  region at  $x < \approx 0.1$ . The 370 K isotherm is for a temperature in between the upper critical endpoint of the low-temperature branch of the liquid-liquid-vapour curve and the lower critical endpoint of the high temperature branch of this curve. So, at this temperature no liquid-liquid-vapour equilibrium is found. However, this isotherm shows an almost horizontal point of inflection, indicating that the system is at this temperature close to a liquid-liquid phase split. The 390 K isotherm is for a temperature in between the lower critical endpoint of the high-temperature branch of the liquid-liquid-vapour curve and the upper critical endpoint of this branch of the liquid-liquid-vapour curve. However, this temperature is higher than the critical temperature of pure 1,1,1,2-tetrafluoroethane. Basically this isotherm is similar to the 350 K isotherm. However the bubble point curve of the  $l_1g$  equilibrium does not end in the pure

component vapour pressure point of 1,1,1,2-tetrafluoroethane, but ends in a binary critical point (not measured).

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## Tables

Table 1. Liquid-liquid equilibria in the system [(1- $x$ ) 1,1,1,2-tetrafluoroethane +  $x$  phenyloctane]: phase boundaries at constant phenyloctane mole fraction  $x$ .

	$T/K$	$P/\text{MPa}$	$T/K$	$P/\text{MPa}$	$T/K$	$P/\text{MPa}$
$x=0.0194$	270.05	0.345	270.96	6.045	272.85	12.045
	270.29	2.045	271.39	8.045		
	270.42	4.045	272.21	10.045		
$x=0.0454$	310.65	1.049	308.59	6.049	307.39	12.049
	309.36	2.049	308.18	8.049		
	308.78	4.049	307.61	10.049		
$x=0.0728$	326.35	1.650	322.32	5.900	320.39	11.900
	325.04	2.650	321.53	7.650		
	323.34	4.400	320.85	9.650		
$x=0.1506$	348.34	2.580	337.79	6.175	333.14	12.056
	344.78	3.188	335.72	8.055		
	341.44	4.207	334.18	10.055		
$x=0.2491$	346.57	3.168	339.38	5.908	334.02	11.993
	352.15	2.453	336.75	8.058		
	343.10	4.118	335.12	10.088		
$x=0.3247$	343.76	2.120	335.23	6.060	331.12	12.000
	340.44	3.060	333.40	8.010		
	338.18	4.060	332.07	10.000		
$x=0.4004$	332.28	2.050	328.59	5.050	326.13	9.050
	330.75	3.050	327.17	7.050	325.37	11.050
$x=0.5001$	312.57	1.005	310.71	5.905	309.73	11.905
	312.07	2.005	310.30	7.905		
	311.29	3.950	309.93	9.905		
$x=0.5861$	292.58	0.910	292.05	4.410	291.95	10.410
	292.51	1.510	291.95	6.410	291.98	12.410
	292.28	2.510	291.92	8.410		
$x=0.7037$	259.36	0.177	259.54	4.057	260.29	10.057
	259.31	0.557	259.92	6.057	260.60	12.057
	259.52	2.057	260.24	8.057		

Table 2. Liquid-liquid-vapour equilibrium pressure in the binary system 1,1,1,2-tetrafluoroethane + phenyloctane

$T/K$	$P/\text{Mpa}$	$T/K$	$P/\text{MPa}$	$T/K$	$P/\text{Mpa}$
283.33	0.426	303.30	0.760	343.38	2.010
293.33	0.574	313.40	0.990	352.85 <sup>a</sup>	2.440
303.30	0.759	323.32	1.280		
313.21	0.999	333.26	1.615		
381.82 <sup>b</sup>	4.220	382.74	4.292	385.27	4.488
381.95	4.231	382.82	4.300	387.30	4.666
382.03	4.237	383.10	4.318	390.11	4.891
382.70	4.288	383.89	4.379	392.88 <sup>c</sup>	5.135

<sup>a</sup> UCEP ( $l_2=l_1$ )g

<sup>b</sup> LCEP ( $l_2=l_1$ )g

<sup>c</sup> UCEP  $l_2(l_1=g)$

Table 3. Vapour-liquid and liquid equilibria in the system [(1-x) 1,1,1,2-tetrafluoroethane + x phenyloctane]: bubble point pressures and liquid-liquid upper solution pressures as function of temperature at constant phenyloctane mole fraction  $x$ .

	$T/K$	$P/MPa$	$T/K$	$P/MPa$	$T/K$	$P/MPa$
$x=0.000$	293.32	0.585	323.25	1.330	353.34	2.651
	298.34	0.680	328.29	1.505	358.40	2.945
	303.32	0.785	333.30	1.695	363.36	3.256
	309.32	0.900	338.26	1.900	368.48	3.615
	313.25	1.025	343.32	2.130	373.38	3.986
	318.31	1.180	348.34	2.380	374.12 <sup>a</sup>	4.044
$x=0.0194$	273.44	0.300	313.57	1.025	353.55	2.590
	283.54	0.425	323.60	1.316	363.62	3.192
	293.47	0.579	333.43	1.665	373.68	3.870
	303.52	0.775	343.66	2.097	382.52	4.475 <sup>a</sup>
$x=0.0454$	313.69	1.011	353.49	2.528	388.81	4.819
	323.50	1.294	363.58	3.088	391.66	5.037
	333.59	1.645	373.71	3.729	393.75	5.223
	343.49	2.054	383.71	4.438		
$x=0.0728$	327.21	1.405	358.17	2.755	388.34	4.755
	337.65	1.795	368.32	3.340	393.29	5.275
	348.06	2.245	378.95	4.000	398.28	5.820
$x=0.1506$	358.31	2.726	382.33	4.262	388.23	4.898
	368.24	3.297	383.25	4.350	393.31	5.449
	378.21	3.959	385.55	4.601	398.30	5.975
$x=0.2491$	353.33	2.488	383.30	4.347	398.46	5.840
	363.32	3.020	387.67	4.703		
	373.37	3.638	392.37	5.220		
$x=0.3247$	344.32	2.085	368.28	3.310	398.32	5.540
	352.04	2.435	378.24	3.950		
	360.27	2.855	388.29	4.695		
$x=0.4004$	333.69	1.640	360.05	2.780	389.91	4.617
	343.32	2.007	369.84	3.318	398.93	5.277
	350.06	2.299	379.90	3.938		

Table 3. continued

	<i>T</i> /K	<i>P</i> /MPa	<i>T</i> /K	<i>P</i> /MPa	<i>T</i> /K	<i>P</i> /MPa
<i>x</i> =0.5001	314.22	1.020	348.28	2.100	388.27	4.025
	318.27	1.125	358.30	2.520	398.30	4.590
	328.25	1.405	368.24	2.980		
	338.31	1.730	378.29	3.490		
<i>x</i> =0.5861	298.46	0.650	338.30	1.590	378.35	3.070
	308.37	0.835	348.35	1.915	388.36	3.490
	318.30	1.055	358.36	2.270	398.39	3.930
	328.27	1.305	368.24	2.650		
<i>x</i> =0.7037	263.56	0.199	298.43	0.551	358.22	1.767
	268.52	0.234	308.26	0.696	368.20	2.032
	273.48	0.277	318.60	0.879	378.14	2.309
	278.35	0.319	328.21	1.061	388.24	2.599
	288.36	0.423	338.31	1.282	398.31	2.864
	292.59	0.474	348.30	1.512		
<i>x</i> =0.8409	268.51	0.166	318.46	0.546	368.32	1.169
	278.40	0.219	328.36	0.653	378.24	1.311
	288.31	0.283	338.42	0.771	388.30	1.456
	298.39	0.362	348.41	0.899	398.22	1.603
	308.33	0.447	358.22	1.030		
<i>x</i> =0.9519	298.48	0.155	338.55	0.277	378.63	0.439
	308.47	0.175	348.57	0.316	388.71	0.483
	318.47	0.206	358.48	0.357	398.75	0.526
	328.41	0.241	368.64	0.399		

<sup>a</sup> critical point (l=g)



### Figure captions:

Figure 1. Liquid-liquid equilibria in the system [(1- $x$ ) 1,1,1,2-tetrafluoroethane +  $x$  heptylbenzene]: liquid-liquid-vapour equilibria ( $\circ$ ), critical endpoint ( $l_2=l_1$ )g ( $\blacktriangle$ ), critical endpoint  $l_2(l_1=g)$  ( $\Delta$ ) and liquid-liquid phase boundaries for  $x = 0.0728$  ( $\bullet$ ),  $x = 0.1506$  ( $\blacktriangledown$ ),  $x = 0.2491$  ( $\square$ ),  $x = 0.3247$  ( $+$ ),  $x = 0.4004$  ( $\blacksquare$ ),  $x = 0.5001$  ( $\nabla$ ),  $x = 0.5861$  ( $\blacklozenge$ ),  $x = 0.7037$  ( $\diamond$ )

Figure 2. Liquid-liquid equilibria in the system [(1- $x$ ) 1,1,1,2-tetrafluoroethane +  $x$  phenyloctane]: isobaric  $T,x$  diagrams

Figure 3. Vapour-liquid and liquid equilibria in the system [(1- $x$ ) 1,1,1,2-tetrafluoroethane +  $x$  phenyloctane]: bubble point pressures and liquid-liquid upper solution pressures as function of temperature at constant phenyloctane mole fraction  $x$ , selected isopleths for  $x = 0.0194$  ( $\bullet$ ), critical point  $x = 0.0194$  ( $\blacklozenge$ ),  $x = 0.4004$  ( $\Delta$ ),  $x = 0.5001$  ( $\blacktriangle$ ),  $x = 0.5861$  ( $\circ$ ),  $x = 0.7037$  ( $\blacktriangledown$ ),  $x = 0.8409$  ( $\diamond$ ),  $x = 0.9519$  ( $\blacksquare$ ).

Figure 4. Fluid phase equilibria in the system [(1- $x$ ) 1,1,1,2-tetrafluoroethane +  $x$  phenyloctane]: isothermal  $P,x$  diagrams.

Figure 1:

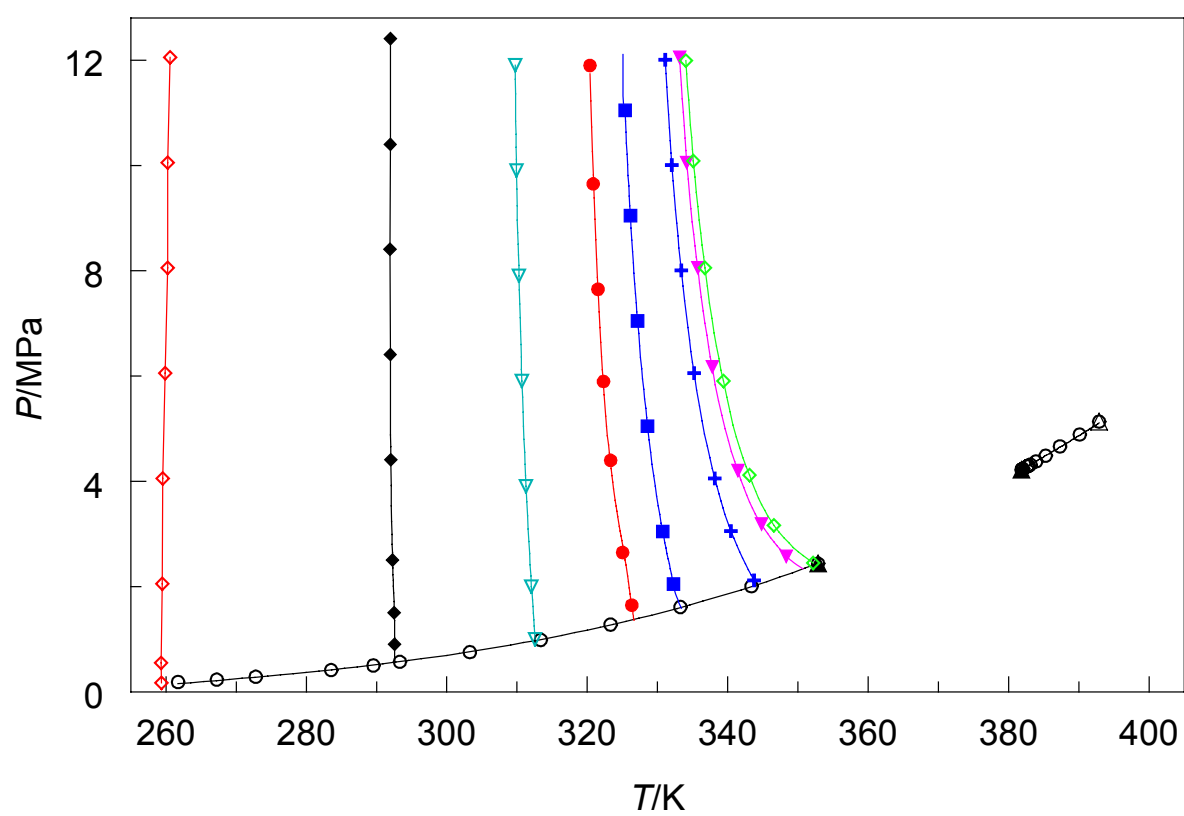


Figure 2:

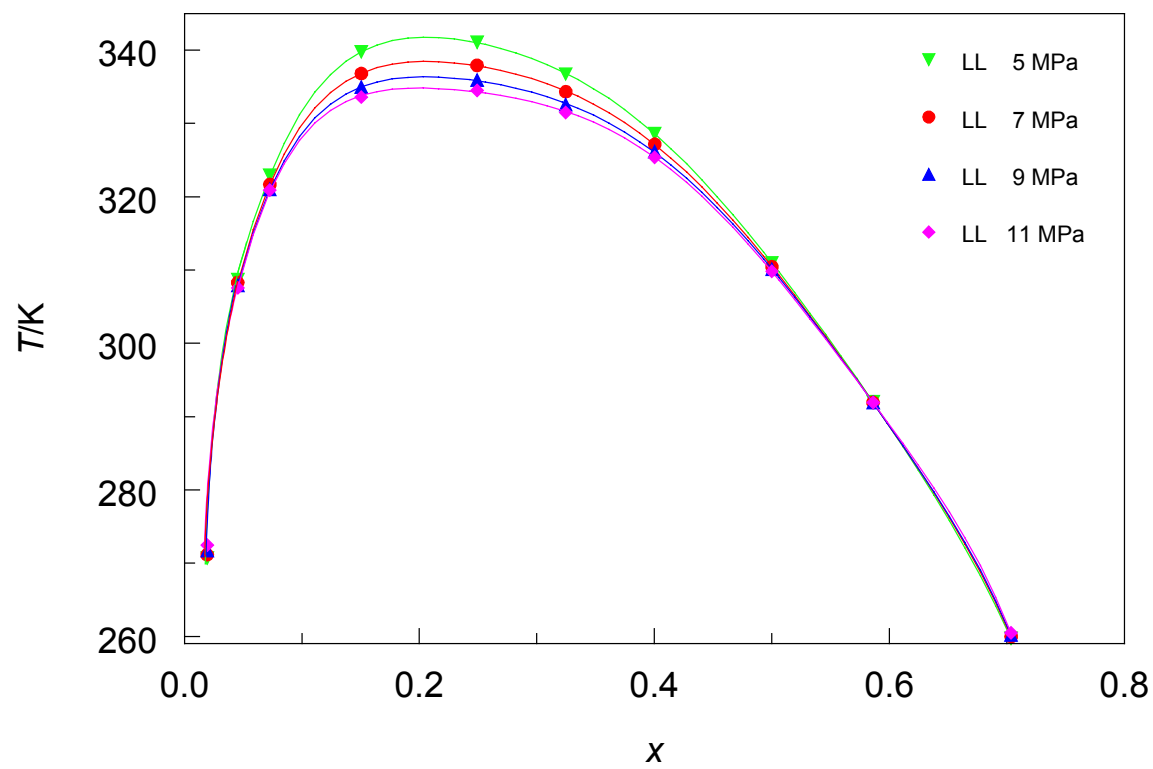


Figure 3:

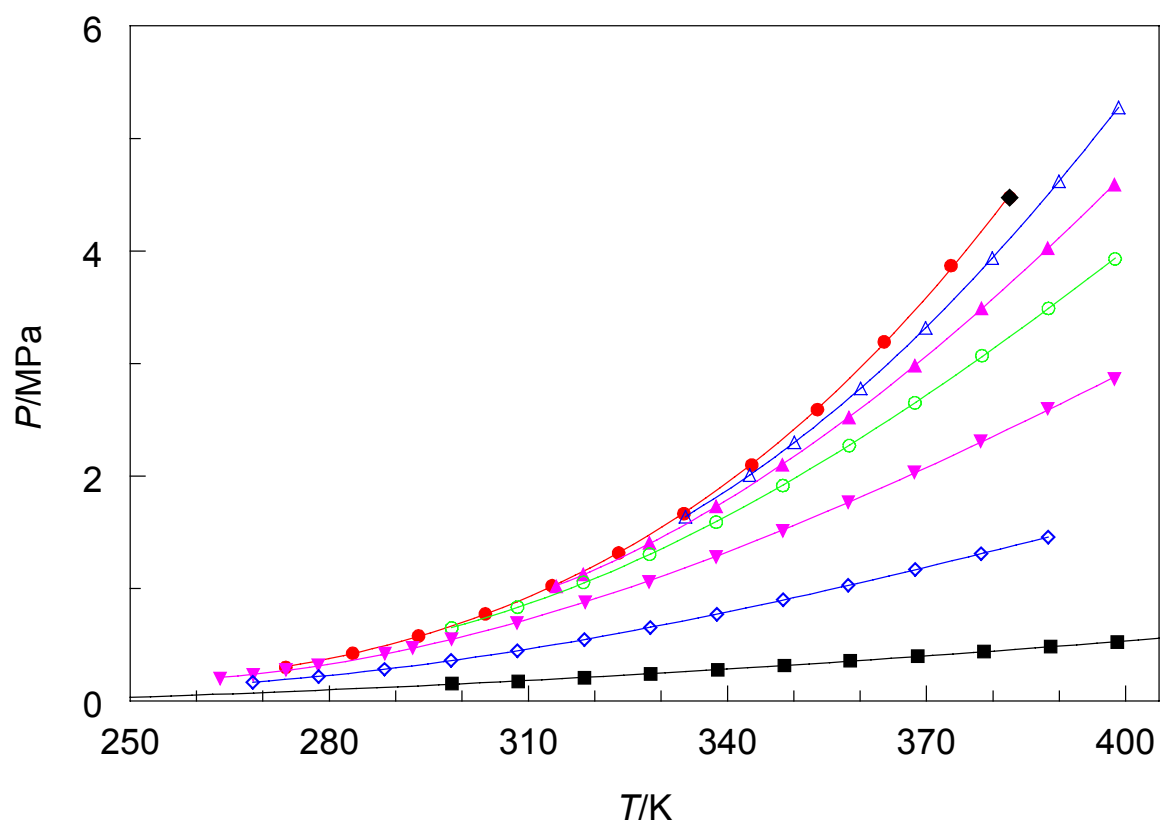


Figure 4:

